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THE TRANSITION TEMPERATURE OF ALPHA TO BETA AMMONIUM NITRATE. SOME METHODS FOR ITS DETERMINATION.

BY

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B. S. University of Illinois, 1922

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Glenn Howe Joseph

ENTITLED The Transition Temperature of Alpha to Beta Ammonium Nitrate. Some Methods for its Determination.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Chemistry.

J. H. Reedy.
In Charge of Thesis

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Head of Department

Recommendation concurred in*

Committee on Final Examination*

*Required for doctor's degree but not for master's

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An expression of sincere gratitude is due Dr.J.H.Reedy for the general encouragement and guidance he has so willingly given throughout the progress of this work.

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THE TRANSITION TEMPERATURE OF ALPHA TO BETA AMMONIUM NITRATE AND SOME METHODS FOR ITS DETERMINATION.

I. INTRODUCTION

The question of transition points, their significance, and the methods for their determination, may be best understood after a general discussion of the cases in which they occur. It has always been evident that when two substances exhibit identical chemical and physical properties, their chemical composition must also be identical. It would not be true, however, to say that when two substances are chemically identical, they always have the same physical properties.

As an example of the last statement, such substances as the diamond and charcoal, ozone and oxygen, may be given. Chemically, the diamond and charcoal are the same - carbon - but their physical properties are different. From this, we see that the elements themselves may exist in more than one modification. Likewise compounds may show such properties. Calcium carbonate, the most common example, exists in many varieties of calcite, which crystallize in the hexagonal system, and also as aragonite, forming crystals in the rhombic system. As early as 1821, Mitscherlich[1] noticed that di-sodium acid phosphate, $Na_2HPO_4 \cdot H_2O$, existed in two distinct crystalline forms.

This property of existing in two or more distinct crystalline forms, when exhibited by an element, is called allotropy, while for compounds it is called polymorphism. Each different crystalline form has a definite set of

conditions of temperature and pressure under which it can exist, and when these conditions are changed beyond a certain limit, that particular form or phase tends to disappear and a new one to take its place. As a matter of fact, these changes do not always take place abruptly at the true transition temperature, with the result that a form may exist in a metastable state outside of its region of stability, in some cases for months and even years. This phenomenon has been designated by Findlay as 'suspended transformation'. Considering the pressure as normal atmospheric, the temperature at which two different forms of an element or of a compound may exist in equilibrium with each other is called the inversion temperature or the transition temperature. For a more complete discussion of transition points and their meanings, reference may be made to the work of Roozeboom. [2]

Transition phenomena are not limited to substances that merely change crystalline shape while retaining the same constitution. There are many acids, bases, and salts that have been found to have the property of entering into combination with water to form definitely constituted crystals. For a given system of a salt and water, there may be several crystalline phases possible. The different crystalline forms in such a case are called hydrates, and their constitution is definite, obeying the ordinary laws of chemical combination. Under certain changes in pressure and temperature such crystals may partially lose their water of hydration to form lower hydrates, or may even go to the

anhydrous salt. These changes in the constitution of hydrates may be considered as reversible, and the temperature at which they occur under ordinary pressure, is called the transition temperature.

There are cases where two or more single salts have combined with one another to form new compounds. These compounds always have the two salts present in simple molecular ratios, sometimes even having water of hydration present in definite amounts. The resulting compound product may in no way resemble either of the constituents in respect to physical properties. There are three possible cases; different salts of the same acid, the same metal with different acids, and different salts of different acids. The formation of a double salt from two single salts is a reversible process. In considering a water solution of a double salt with the same acid radical, it is found that the system is univariant, or that at a given pressure there is only one temperature possible at which all four phases present may be in equilibrium.Such a temperature is also called the transition temperature.

In any case where a change in crystalline form or a change in hydration occurs, or in one of mixed salts, the phase rule may be applied to ascertain whether or not such a system should, when under a fixed pressure, have a temperature of equilibrium, and hence a transition point.

II. HISTORICAL AND THEORETICAL.

As soon as Mitscherlich [1] in 1821, found that sodium phosphate could exist in two different crystalline modifications, chemists became interested in methods for the accurate determination of the transition points. It was soon found that the physical properties of the polymorphs differed. All the present methods for the determination of transition temperatures depend on the fact that some physical property undergoes a change at the transition point. There have been many properties studied to find a suitable method for such a determination. Probably the best known method depends on the volume change, and is known as the dilatometer method.

(1) Dilatometric Method.

It was found that when transition took place between two crystalline phases there always resulted a volume change. It follows from the principle of Le Chatlier that the form stable at the higher temperature has the greater volume. It is evident, then, that the determination of the temperature at which an unusual change in volume occured, would give the transition point of the two phases. The instrument used to detect the volume change is called a dilatometer. The form used at the present time is exactly as described by van't Hoff in 1887,[3] and used many years before. It consists of a bulb connected to a long capillary tube to resemble an oversized thermometer. The making of one is not such a difficult task, but the filling of one is a very tedious and sometimes an

impossible undertaking. In making a determination by such an apparatus, the item of greatest concern is to get the material to be tested into the bulb of the dilatometer, covered with a liquid that does not dissolve in it, and in which the material has practically no solubility, and at the same time introduce no air bubbles or heat the bulb to a temperature within a range dangerous to the experiment at hand.

After all the preliminary adjustments have been made, the bulb is immersed in some type of bath in which it may be heated at a slow and uniform rate. Usually a large beaker or pail of water will do if there has been made ample provision for stirring. The temperature of the bath may be either higher or lower than the supposed transition point, and then all that is necessary, is to proceed as in making a cooling or heating curve, plotting the height of the liquid in the tube against the temperature of the bath. Usually the plotting was not necessary, as the increase in volume at a certain temperature was great enough to be easily observed during the determination. Of course the relation between the temperature and volume increase will be uniform unless there is a volume change in the material within the bulb.

Another method sometimes used in dilatometer determinations is based on the fact that on either side of the transition point, the unstable phase tends to pass into the stable phase, but at the transition temperature both may exist side by side in equilibrium. Hence if the bulb was charged with a mixture of the two modifications of a salt and immersed in a bath of constant temperature and an expansion or

contraction took place, it is evident that the temperature was not the one of equilibrium. The temperature of the bath is then changed until there is neither expansion or contraction, showing that it is at the true transition point. This method is not always applicable and is a very hard one to manipulate accurately, hence it is seldom used at the present time.

(2) Thermometric Method.

It is a familiar fact that when a solid is heated not too near its melting point, the temperature rise is uniform, but at the melting point the temperature of the substance can not be raised until the solid phase has completely disappeared. This has also been found to hold for substances that exhibit transition phenomena. From the phase rule, $F = C + 2 - P$, it is evident that this should be the case. For example, ammonium nitrate will be used, the dry salt being heated in a tube open to the atmosphere. The number of phases will be three, the alpha and beta solid forms, and a vanishingly small amount of a vapor form, and since there is only one component, the degrees of freedom will be, $1 + 2 - 3$ or 0. Such cases as this, however, in which the concentration of the vapor phase is negligible, are best considered from the standpoint of what van't Hoff has called "condensed systems". For such systems where the densities of the solid and liquid phases are very little affected by changes in pressure, the transition temperature determined in an open vessel at atmoshperic pressure will differ only by a slight amount

from the true transition point; that is, the point at which the two solid or liquid phases are in equilibrium under the pressure of their own vapor. For such systems, then, the vapor phase may be neglected, and a modified form of the phase rule may be used: $F = C + 2 - 2$ (for condensed systems). In the case of the alpha and beta forms of ammonium nitrate in equilibrium with each other, the degree of freedom will be zero; that is there can be only one temperature at which both the phases may be in equilibrium. Hence, since the change from one to the other is not instantaneous, all that is needed is to heat the material in a test-tube and note the place where the temperature will not increase even though the heat is applied as usual. This will be the temperature of equilibrium.

This method was used by van't Hoff in 1895 for the determination of the transition points of sodium and potassium tartrates.[4] T.W. Richards and his associates, Churchill[5], Kelly[6], and Wells[7], used this method with very elaborate modifications for the determination of transition points of the various hydrates of such salts as sodium bromide, sodium sulfate, manganese chloride, and sodium chromate. No reference was found in the literature where this method was used on a compound other than a complex or hydrated salt.

(3) Solubility Measurements.

When a substance such as ammonium nitrate is at the transition point, there is no tendency for one form to change to the other, their difference in free energy is zero, each

form is in equilibrium with its vapor, and hence the two forms must have the same solubilities at the transition point. As the temperatures of the different forms diverge from the transition point, their difference in free energy becomes greater, and their physical properties become more noticeably different. From this it is apparent that the solubility curve for a polymorphic substance can not be a straight line over the range of temperature including its transition point. By plotting the solubility curve, any breaks will be indices of transitions. Müller [8] in 1899, and Müller and Kaufmann [9] in 1903, used this method for the determination of the transition point of ammonium nitrate. The correct temperature of transition is difficult to determine by this method. Van't Hoff [10], and Meyerhoffer and Saunders [11], have designed special forms of apparatus for the determination of solubilities.

(4) Vapor Pressure Methods.

From the preceding discussion it is evident that vapor pressures of the two forms of a polymorph must be identical at the transition temperature. Hence by plotting the vapor pressure of a substance over a range in temperature, it is possible to notice the breaks in the curve due to transitions. The application of this method has never been made to a one component system. For the determination of the vapor pressure of hydrates, the Bremer-Frowein [12] tensimeter is used.

(5) Electromotive Force Methods.

These methods depend on the fact that when electrodes

of the same material are immersed in electrolytes of different concentrations, there will be a small electromotive force shown. Thus if two Clark cells were used, [$Zn:ZnSO_4$(sat. solution):Hg_2SO_4 : Hg.] one filled with a solution of the heptahydrate and the other the hexahydrate of zinc sulfate, each at a different temperature, the electromotive force will be dependent on the difference in temperature of the two cells. The electromotive force will not be zero except at 39°C where the two salts have their transition point. At this temperature the salts have the same solubility and the solutions are of the same concentration. Such reactions may involve only the electrolyte, or they may involve changes in the electrodes themselves. The transition point for grey and white tin, found by van't Hoff, is an example of the latter case. Many varieties of transition cells have been described by van't Hoff and Cohen.[13]

(6) Optical Methods.

There are several instances where the temperature of transition of crystalline compounds and double salts has been determined by observing an alteration in crystalline form or color by means of a microscope. Some solutions exhibit color reactions at the transition point. A concentrated solution of ferric and potassium chlorides below 22°C is yellow while above that temperature it is red, due to the salt, $FeCl_3 \cdot 2KCl \cdot H_2O$.[14]

III. THE TRANSITION OF AMMONIUM NITRATE.

The transition of ammonium nitrate is one in which no water of hydration is concerned, there only being a change in crystalline form. The transformation of the crystalline forms can be observed with either ascending or descending temperature,- that is, it is an enantiotropic change. The form existing below 30°-35°C has been called alpha rhombic, while from 35° to 85° it is called beta rhombic. Above 85° and below 125° it is rhombohedral. Abegg [15] has differed, for he calls the lowest phase the beta rhombic and the one from 35° to 85° the alpha rhombic. The salt is very easy to obtain in the pure state. The transition temperature is just high enough that the salt may be re-crystallized at ordinary laboratory temperatures for the lower modification, and still it is not high enough to cause trouble in the determination of the correct point.

Up to the present time the transition temperature of alpha to beta ammonium nitrate has not been satisfactorily determined. From Table 1a, taken from Landolt-Börnstein [16] with the exception of the last mentioned result, shows the various results reported.

TABLE 1a.

Temperature	Observer	Method
36.0°	Lehmann	Optical
31.0-35.0°	Romanese	Thermometric
35.0°	Romanese	Dilatometric
31°- 35°	Schwartz	Dilatometric
32.4°	Preissher	Optical
32.2°	Müller	Solubility
35.0°	Boks	Thermometric
35.0°	Zawidshi	Thermometric
32.0°	Lowry	Solubility [17]

All these facts made ammonium nitrate an ideal substance to use in a study of methods for the determination of transition points. It has its drawbacks, however. Ammonium nitrate might be regarded, not only as a component in explosives, but as a dangerous explosive in the free state. Consider the equation for its decomposition to be;

$$NH_4NO_3 \text{ (solid)} = 2H_2O \text{ (gas)} + \tfrac{1}{2}O_2 + N_2$$

Lewis and Randall [18] have calculated the change in free energy for the aqueous solution at 298°K (i.e. 25°C) to be -63,600 cal. This appears to put solid ammonium nitrate in the class with the dangerous explosives if improperly handled. For all ordinary uses, however, this material has been found stable and thoroughly safe. The greatest amount of work concerning the physical properties of the various modifications of ammonium nitrate, was done by Bellati and Romanese[19]. They calculated the specific heats, the rates of expansion, and the heats of transition.

It is evident from the discussion that the true transition temperature, up to this time, has never been determined. The different methods for its determination give results that are so widely different as to be worthless. An attempt to determine the exact temperature of the transition and at the same time to study the different methods to see where they may be at fault and may be improved, then, seemed to be worth while, and so was made the object of this thesis.

IV. EXPERIMENTAL

(1) Apparatus.

For a complete study of such a problem, a heating bath whose temperature may be controlled accurately, is of course necessary. For the purposes of this problem,a water bath was suitable.The apparatus was set up as shown in Figure 1. The glass jar, the container of the thermostat, was of about fifteen liters capacity, and was covered with a thich layer of hair-felt insulation.

The heat for raising the temperature of the water bath was furnished by two electric lamps, one a fifty candle power carbon filament lamp, and the other, a nitrogen filled lamp of 100 watt size. These were connected in parallel, and, through a relay, with the lighting circuit. Two large lamps were connected in series and shunted across the relay points to keep down the excessive sparking and the resulting sticking of the points of the relay. The smaller of the lamps was of such intensity that it heated the bath at the rate of 0.040°C per minute, at room temperature. For the greater part of the work, only the carbon filament lamp was used.

The relay was actuated by the usual type of thermoregulator. The usual platinum point connection in a capillary tube was used for adjusting the temperature. The bath was continually stirred by means of a five inch brass propellor operated by a small electric motor. The arrangements were sufficiently accurate and sensitive to maintain the bath at a temperature within 0.02° constant for long periods.

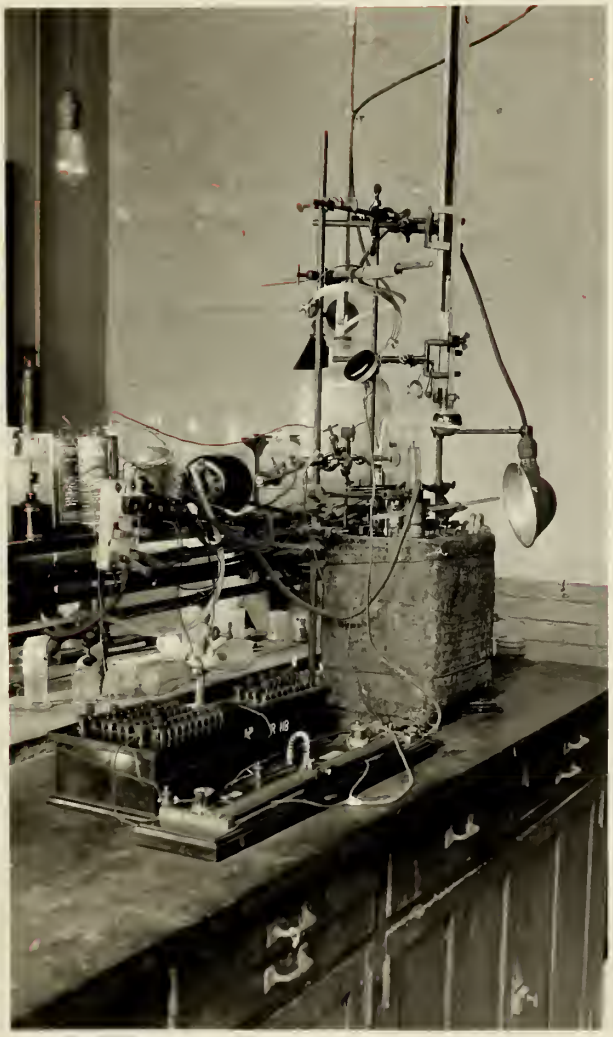


Figure 1.

For cooling at a regular rate, faster than by radiation, cold water was allowed to trickle through a lead coil which was fastened to one of the inside walls of the jar. A large bottle was placed on a shelf over the apparatus. In this bottle, water from the faucet was allowed to trickle over crushed ice and then out through a valve to the coil. By adjusting the outlet from the bottle the temperature of the bath could be lowered at any desired rate. Large stay rods were bolted in various places from the jar and the uprights to the table and desk to prevent any motor vibration from shaking the apparatus.

The thermometers used in this work were carefully selected for accuracy and length of scale. After six were selected as suitable, they were compared with a standard, and their correction curves plotted. The thermometers used as standards were made by Siebert and Kühn, of Cassel, and were calibrated by the Physikalische-Technische Reichsanstalt under numbers PTR- 27094 and PTR- 27095. The thermometer used in most of the work was of an American make and was calibrated over a range from 20° to 35°C. The scale divisions were of such length that by the aid of an ingenious reading lens, similar to the ones used with calorimeters, temperatures could be read to 0.005° with sufficient accuracy. The thermometers were compared with the standard by immersion in a Dewar flask until constant readings were obtained, and the water in the flask slightly heated and the process repeated.

(2) Materials.

The materials used as chemicals were of the "C.P." grade from our best manufacturers. In the case of the sodium sulfate, it was recrystallized from water at 25° just previous to use, to insure the correct hydrate. The ammonium nitrate was taken to be of sufficient purity and likewise the urea and sodium nitrate. Some ammonium nitrate was made at first and its constants were taken and found to be identical with the pure product that was commercially obtainable. The ammonium nitrate was stored in tightly stoppered bottles away from the light and at a temperature of approximately 23°C. The kerosene used was carefully dried by distillation and by the use of calcium chloride.

(3) Preliminary Dilatometer Determinations.

The first determinations made were simple experiments following the directions laid down by the standard texts for the determination of transition points by the dilatometer method. The dilatometer was made as suggested in all the books. A capillary tube of approximately 2mm. bore was sealed at one end and then the end blown into a bulb of about ten or fifteen cubic centimeters capacity. The finely pulverized ammonium nitrate was introduced through the capillary. It was soon found that this type was worthless from the standpoint of ease of making, and operation. The other type discussed in text-books was tried. A large tube was sealed on a capillary tube, and then inverted so the capillary was down, with the opening in to it closed by a glass bead. The material to be

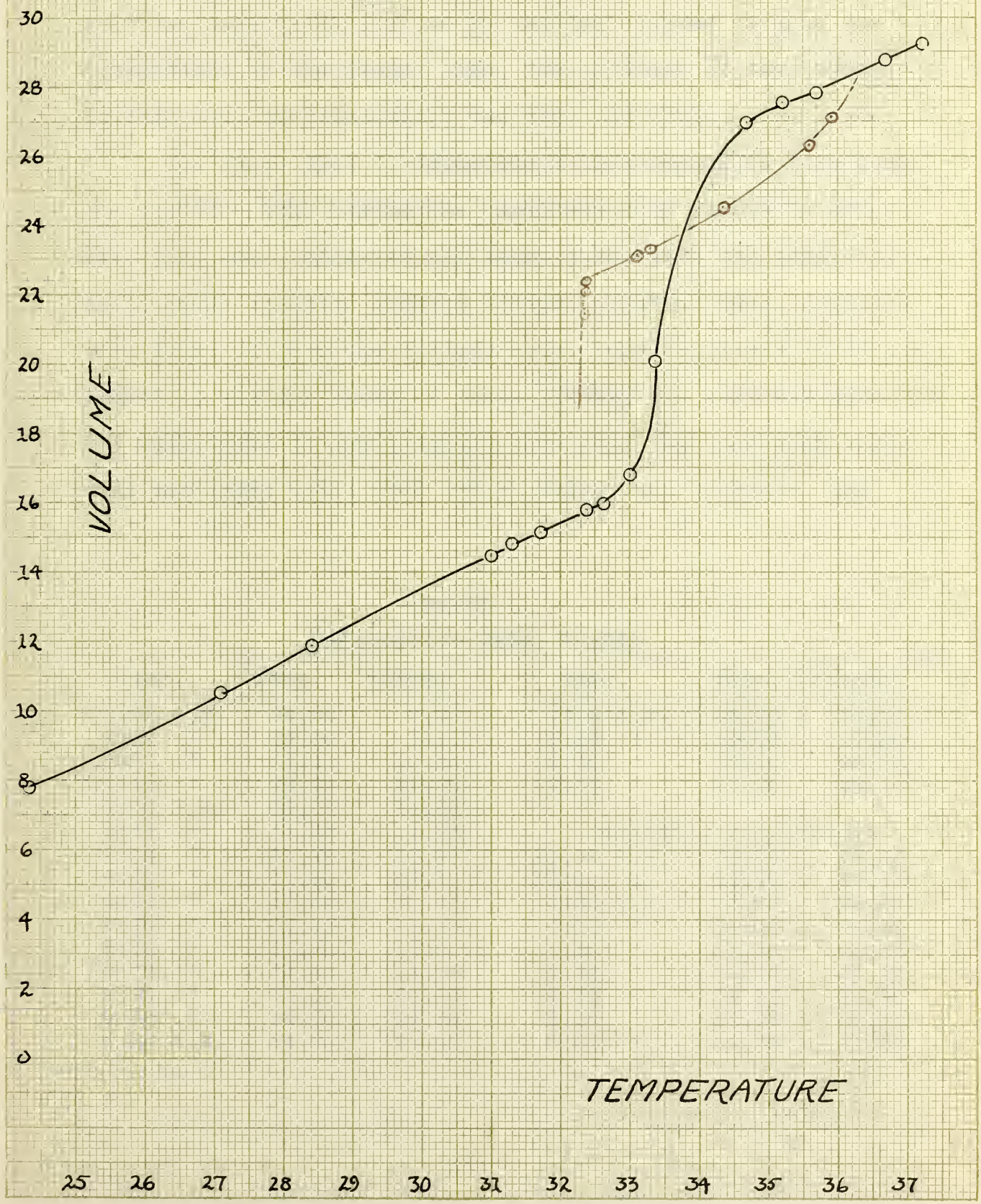
PLATE I

TRANSITION CURVE

AMMONIUM NITRATE

25 HOUR RUN

10/19/22



used was then introduced and the large tube sealed off. The liquid was then introduced and the determination carried out as usual. The trouble experienced with this type was that the salt was made unfit for use by the heat needed to make the alterations in the glass. Also, the addition of any liquid to this type of dilatometer was very difficult.

The first type of improvement that suggested itself was the use of a bulb having the capillary tube removable and a neck that would allow an air tight joint with the capillary used. Small specific gravity bottles of about 50cc. capacity were found to have the desired neck. Long capillary tubes were ground to fit the necks of these flasks. The salt was added to the bulb until it was slightly over half full and then kerosene was added until when the capillary was inserted, the

TABLE 1.

Dilatometer Data. NH_4NO_3

Time.	Temp.	Volume.
8:55 A.M.	24.30	7.45
9:25 "	24.30	7.45
10:37 "	27.10	10.50
11:55 "	28.40	11.80
2:00 P.M.	30.95	14.50
3:45 "	31.35	14.75
4:00 "	31.70	15.05
4:40 "	31.80	15.10
4:55 "	32.35	15.65
5:20 "	32.35	15.75
5:30 "	32.60	15.90
8:40 "	33.00	16.65
9:20 "	33.35	20.15
9:48 "	34.70	26.50
6:50 A.M.	34.70	27.00

Time.	Temp.	Volume
7:10 A.M.	35.20	27.50
8:15 "	35.70	27.80
8:40 "	36.70	28.75
9:55 "	37.20	29.10
Decending Temperature		
10:55 A.M.	35.80	27.40
12:00 M.	35.90	27.15
3:35 P.M.	35.60	26.25
4:08 "	34.35	24.55
4:30 "	33.30	23.35
4:45 "	33.10	23.10
4:55 "	32.35	22.30
5:10 "	32.35	22.15
8:25 "	32.35	21.55

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level of liquid came within the desired range on the scale on the capillary tube. The air that was mechanically held in the salt and the kerosene was removed by attaching a vacuum before inserting the capillary tube. Beeswax was used to make certain that the joint was tight. Such an apparatus gave results as shown in Table I and on Plate I.

The dilatometer was suspended in the thermostat and the temperature held constant until the level of the kerosene in the capillary tube remained constant. The temperature of the bath was slightly raised and the same procedure followed as before. The temperature was held constant over night. The rate of increase in volume with the temperature was not so great at any one temperature as to be noticeable, contrary to expectations. After twenty five hours had elapsed and the temperature had been raised twelve degrees, the lamps were turned off and the cooling started. After nine and a half hours the bath had cooled four degrees. In Table 1 only a portion of the data from the original data sheet is given.

Table II.

DILATOMETER METHOD. ROCHELLE SALTS.

Volume	Temperature		Volume	Temperature
23.50	52.10		28.30	55.44
24.30	53.07		29.50	55.71
25.10	53.95		32.20	56.11
25.85	54.45		36.00	56.20
26.15	54.60		36.50	56.25
26.70	55.00		38.05	56.60
27.00	55.08		41.50	57.65
28.00	55.40		44.10	58.10
First reading at 10:20 A.M. Last reading at 8:30 P.M.				

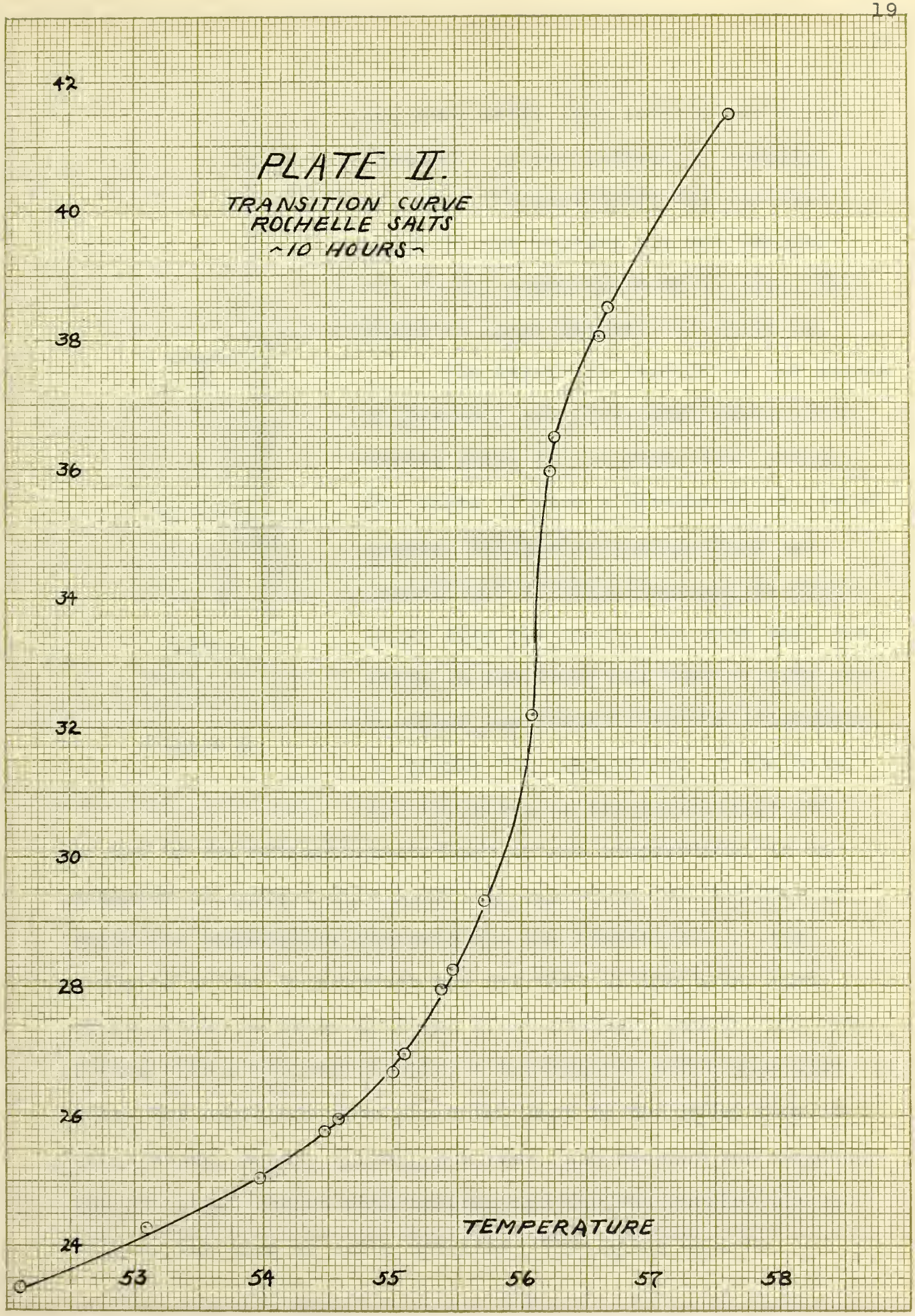
PLATE II.
TRANSITION CURVE
ROCHELLE SALTS
~10 HOURS~
42
40
38
36
34
32
30
28
26
24
53
54
55
56
57
58
TEMPERATURE

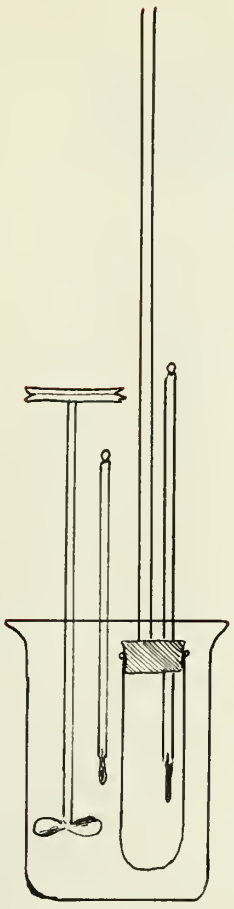

Figure 2.

The same method was carried out using "Rochelle Salts" instead of ammonium nitrate. The experiment was run over a range of six degrees and was carried out in ten hours. The data is shown in Table II (page 18) and on Plate II.

The important feature of the curves in Plates I and II is that there is no marked break at the transition point. The value of such a determination is, of course, the accuracy with which the temperature of transition may be determined from the curve. The time that was taken in the tests was surely sufficient to allow the contents of the dilatometer to assume the temperature of the bath, and the shape of the curve could not be due to the oft-mentioned "lag" in the temperature. In an endeavor to correct this fault, an apparatus was designed in which the temperature observed was the temperature of the contents of the dilatometer and not that of the bath. Such an apparatus is shown in Figue 2. An ordinary sample tube was fitted with a stopper carrying a thermometer and a capillary tube. The capillary tube projected just to the under side of the stopper. After filling the tube, the stopper was inserted and the joint sealed with beeswax and the run carried out as before. The type of curve resulting from using such an

PLATE III

TRANSITION CURVE

AMMONIUM NITRATE

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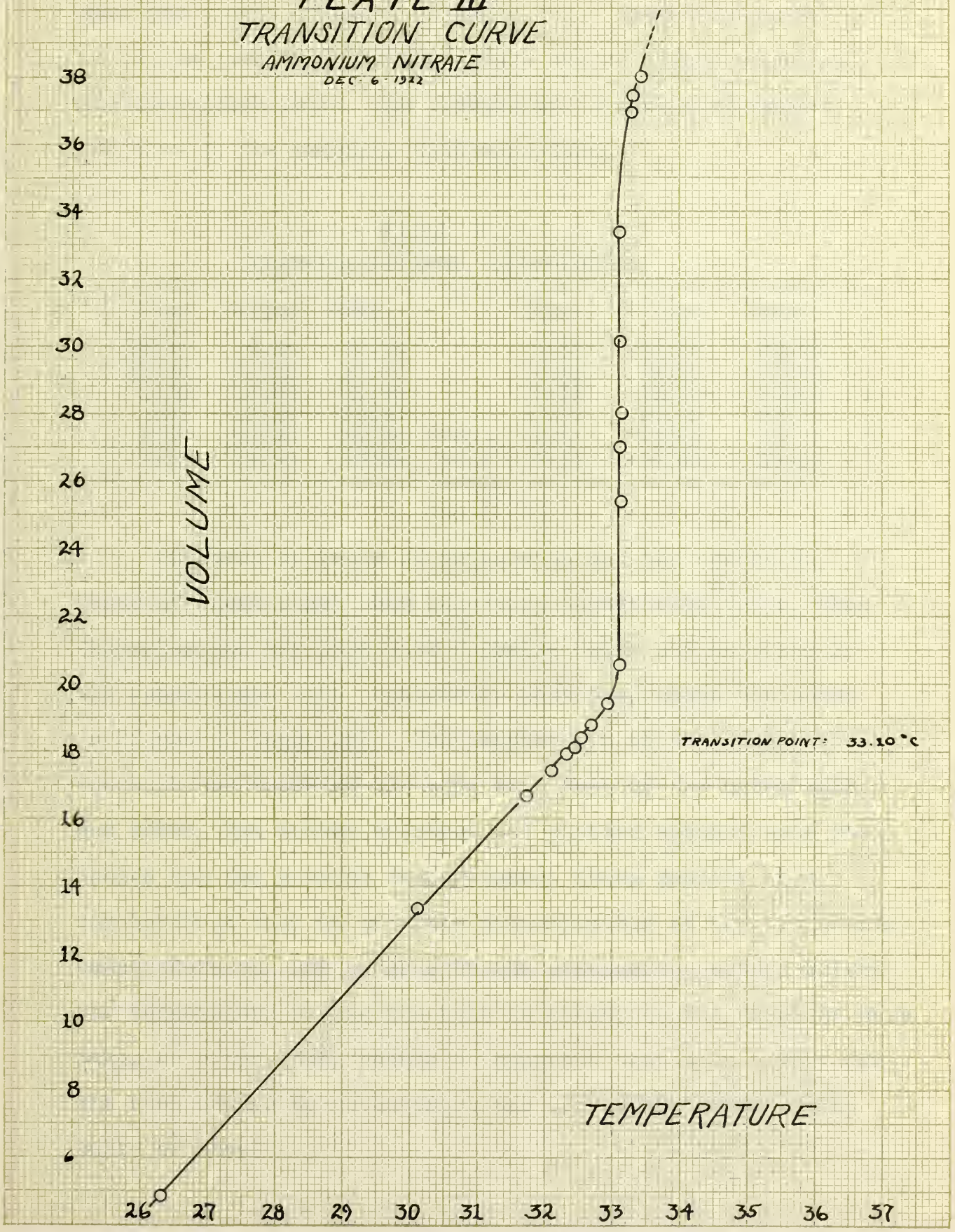


apparatus may be seen in Plate III (page 21), part of the data for which, is given in Table III. From this curve it can be seen that although there was no abrupt break at the transition point, the flexure was a much more marked one than in the previous determinations.

TABLE 3.

AMMONIUM NITRATE. DILATOMETER.

Time	Volume	Temp.	Time	Volume	Temp.
10:10	4.80	26.30	2:24	19.15	32.80
11:40	13.40	30.05	3:00	20.40	32.90
1:30	16.65	31.70	3:35	25.50	33.10
2:01	18.10	32.40	4:00	30.20	33.10
2:07	18.40	32.50	4:30	33.40	33.10
2:13	18.80	32.70	5:15	38.60	33.60

The data in Table IV on page 24 and the curves on Plate IV (next page) show some very significant facts. This determination was made with Rochelle Salts and kerosene in the sample-tube type dilatometer mentioned above and shown in Figure 2 (page 20) , The temperature on the inside of the bulb was taken at the same time that of the water bath was taken, The volume increase was plotted against both the inside and the outside temperatures. These results show conclusively that an accurate determination of the transition temperature can not be made by the dilatometer method unless the temperature within the bulb is known. As the readings were taken so often, they became so numerous that only a very few , the ones needed to reconstruct the curves,are given in the table of data.

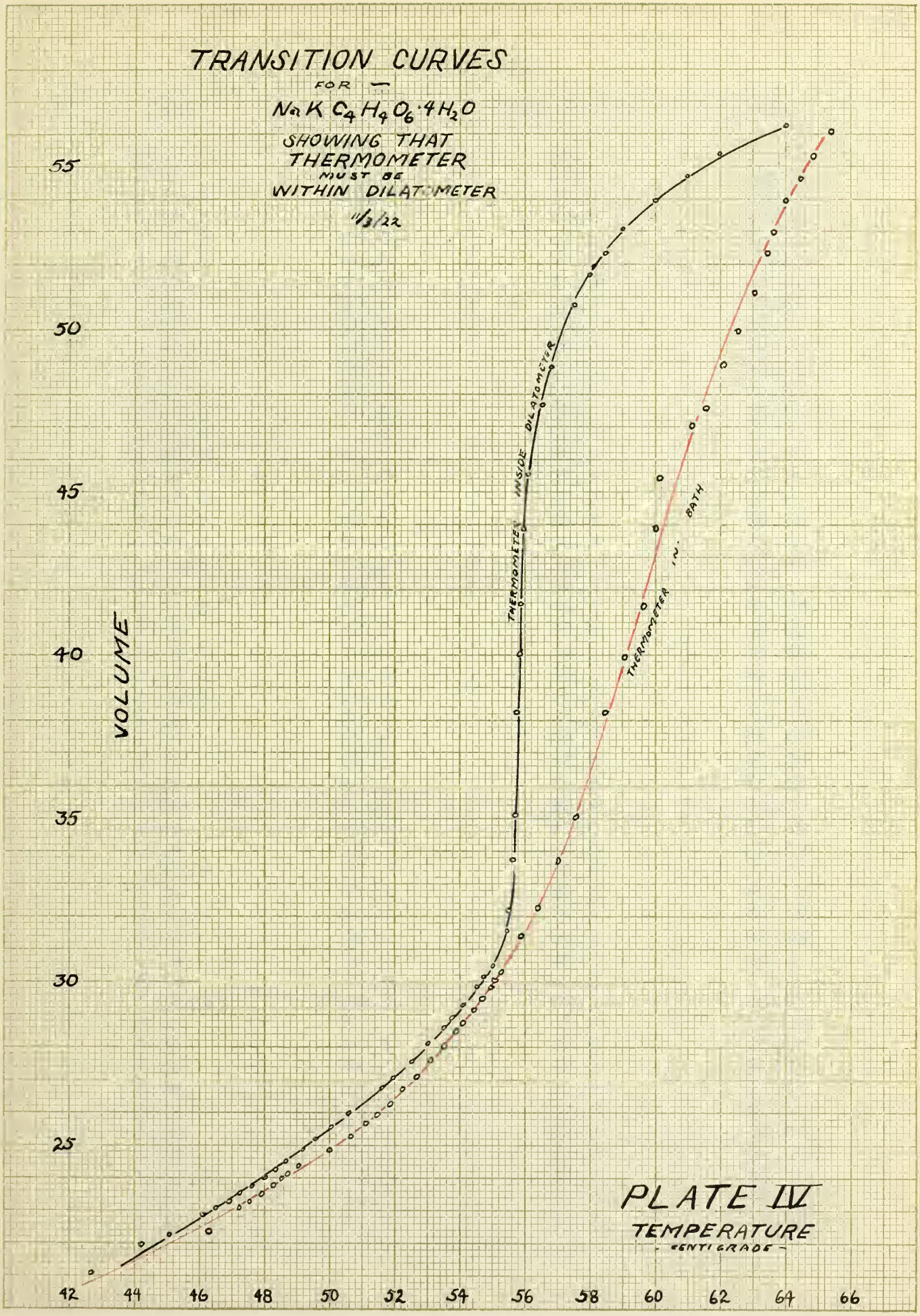

TRANSITION CURVES
FOR —
$NaKC_4H_4O_6 \cdot 4H_2O$
SHOWING THAT
THERMOMETER
MUST BE
WITHIN DILATOMETER
11/3/22
55
50
45
40
35
30
25
VOLUME
INSIDE DILATOMETER
THERMOMETER
THERMOMETER IN BATH
42
44
46
48
50
52
54
56
58
60
62
64
66
PLATE IV
TEMPERATURE
- CENTIGRADE -

Table IV.

Time	Temp. Outside	Temp. Inside	Volume
3:18	42.6	44.5	21.15
3:21	44.1	45.9	22.00
3:22.5	45.0	46.1	22.30
3:25.5	46.0	46.8	22.90
3:27.5	46.5	47.1	23.10
3:29.7	46.8	47.5	23.33
3:31.5	47.2	47.9	23.55
3:33.5	47.6	48.2	23.80
3:38	48.2	48.6	24.20
3:40.5	48.6	49.0	24.50
3:44	49.0	50.0	25.00
3:45	49.5	50.6	25.25
3:47.5	50.0	51.0	25.70
3:50.5	51.0	51.8	26.35
3:53.5	51.5	52.2	26.80
3:56	52.0	52.6	27.20
3:58.5	52.5	53.0	27.6
4:02.5	53.0	53.5	28.10
4:06.5	53.5	53.8	28.60
4:08.5	53.7	54.0	28.83
4:10	53.8	54.3	29.10
4:11.5	54.0	54.4	29.25
4:15	54.5	55.0	29.80
4:16.5	54.6	55.0	30.00
4:17.5	54.7	55.1	30.10
4:18.5	54.9	55.2	30.25
4:20	54.9	55.2	30.35
4:24	55.0	55.4	30.65
4:30	55.2	55.5	31.20
4:34	55.4	55.8	31.50
4:39	55.5	56.4	32.30
4:44	55.6	57.0	33.70
4:48	55.7	57.6	35.10
4:55.5	55.7	58.5	38.30
4:59	55.8	59.0	40.15
5:02.5	55.9	59.7	41.55
5:07	56.0	60.0	43.85
5:09	56.1	60.1	45.5
5:14	56.5	61.6	47.6
5:16.5	56.8	62.1	48.9
5:19	57.3	62.6	50.05
5:20	57.5	62.8	50.80
5:23	58.0	63.1	51.70
5:24	58.5	63.5	52.40
5:26	59.0	63.6	53.10
5:29	60.0	64.0	54.00
5:31	61.0	64.5	54.70
5:33.5	62.0	64.9	55.40
5:37	64.0	65.4	56.20
5:41	65.0	66.0	57.00

Nov. 3 1922

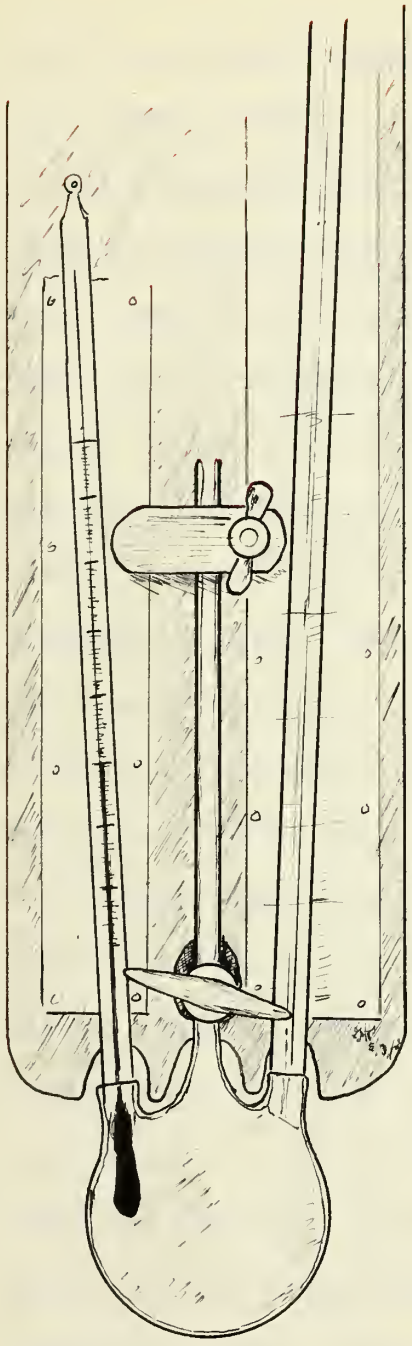


Figure 3.

(4) Effect of a Dye in Liquid for Dilatometer Determinations.

An experiment designed to determine ~~the~~ the effect of a dye in the kerosene on the transition of ammonium nitrate was carried out using the tube-type dilatometer as described. An oil soluble dye, Sudan III, was used in the oil until it had assumed a very noticeable red color. The run lasted from 2:30 P.M. October 23,1922 until 5:50 P.M. the following day. The data and curves for this are not given, but the temperature found for the transition was 33.02°C., after corrections had been applied for the thermometer. This checked satisfactorily the temperatures determined in previous cases without the dye, and hence the dye was used in all the determinations following, making it easier to read the heights in the capillary tube.

(5) Improved Dilatometer Method.

After considering the advantages and disadvantages of the dilatometer previously used, the apparatus shown in Figure 3 was constructed. The volume of the bulb was about

75 cc. Both the thermometer and the capillary tube were carefully ground to fit the necks in the bulb. The projecting end of the stop-cock was fitted through a hole in the board shown to support the weight of the apparatus. The joints were covered with beeswax and were found to be non-leaking. This type of apparatus was very easily filled. The bulb was nearly filled with kerosene before the tubes were inserted and then the remainder added through the stop-cock tube. By having a small rubber tube attached to the central tube, and blowing slightly, the level of the kerosene in the capillary could be adjusted at will. The advantage of this may be seen if it was desired to make a run where the temperature needed was around 75°C. The old type dilatometer, when filled at room temperature and then immersed in water at a temperature near 75°C, would show an increase in volume so great as to be out of range on the scale. With the new type, it would be possible to keep the stop-cock open until the temperature had been raised to the desired starting point and then the level could be adjusted to the zero on the scale. This also does away with the exceedingly heavy columns in the capillary that might cause error. Here when the liquid gets too high in the capillary tube, it may be lowered and the amount of lowering added to the following readings with adding any error. Any bubbles that might form from any reason during the run would rise to the highest place in the bulb, here, under the stop-cock, where they could do no harm. In the other type of dilatometer they would get to the capillary and sometimes

escape, causing errors in the readings.

Very satisfactory results were obtained from using this type of apparatus, as may be seen from the curves on Plate V. (page 28). The data for these curves is in Table V.

Table V. (a)

Ammonium Nitrate. Sodium Nitrate.
Nov. 27 1922

Time	Volume	Temp.	Time	Volume	Temp.
3:04	5.15	25.21	5:50	23.70	33.34
3:45	10.00	27.35	6:02	25.70	33.40
5:20	22.20	32.83	6:18	28.60	33.40
5:25	22.60	33.10	8:35	32.50	33.40
5:35	22.90	33.20	9:03	35.00	34.40
5:39	23.25	33.26	9:15	38.00	35.40

(b)
Dec. 4, 1922

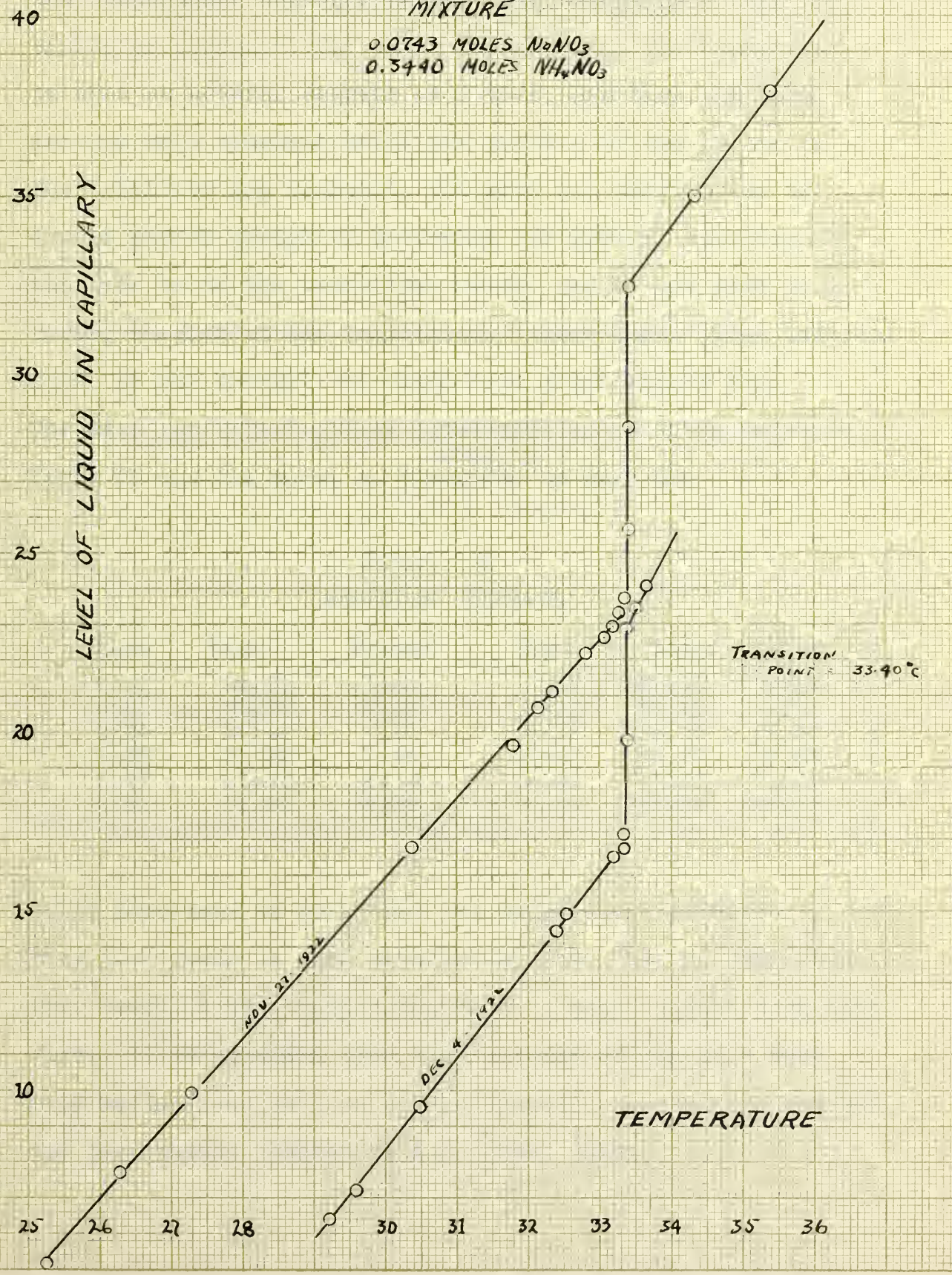
Time	Volume	Temp.
11:50	6.45	29.21
1:40	7.25	29.60
1:45	9.50	30.50
2:30	14.50	32.40
3:20	15.00	32.55
3:45	16.50	33.20
3:50	16.80	33.35
3:55	17.25	33.40
4:07	19.85	33.40
4:23	23.00	33.40
4:30	23.50	33.50
4:45	26.10	33.70

The bulb contained in this case, not pure ammonium nitrate, but a mixture of it with sodium nitrate, the amounts of each designated on the plate. It is for the general appearance of the curve that it is shown, but it is to be noticed that the temperature of transition is 0.40° higher in each case than when pure ammonium nitrate is used alone. Mention of this will be made at a later point.

PLATE V

TRANSITION CURVES FOR AN AMMONIUM AND SODIUM NITRATE MIXTURE

0.0743 MOLES $NaNO_3$
0.3440 MOLES NH_4NO_3



One determination was made to ascertain how rapidly the temperature could be raised, still keeping within the bounds of accuracy. Hot water was added to the thermostat to heat it several degrees at a time, and then the temperature held constant until the reading of the liquid in the capillary was constant. All that was desired was to obtain points enough to determine the general direction of the line below the transition point, and to get some points during the rise at the transition. Where these lines intersected, it was thought the transition point should lie. The data for this two hour determination is given below in Table VI and the curve on Plate VI on page 30.

TABLE 6

AMMONIUM NITRATE

Time	Temp.	Volume	Time	Temp.	Volume
2:00	25.50	-1.80	2:53	33.43	8.60
2:11	28.70	2.30	3:00	33.40	9.50
2:24	30.80	4.86	3:37	33.26	19.48
2:38	33.00	7.50	3:42	33.27	19.62
2:47	33.35	8.18	3:58	33.35	23.20
2:50	33.42	8.32	4:06	33.35	24.00

It is important to note that the temperature obtained is a very good check to that obtained by runs lasting over twenty four hours. A very surprising fact is made evident from this curve. It is apparent that the contents of the bulb were superheated, and as soon as the transition point was reached, the temperature lowered to its normal value.

PLATE VI

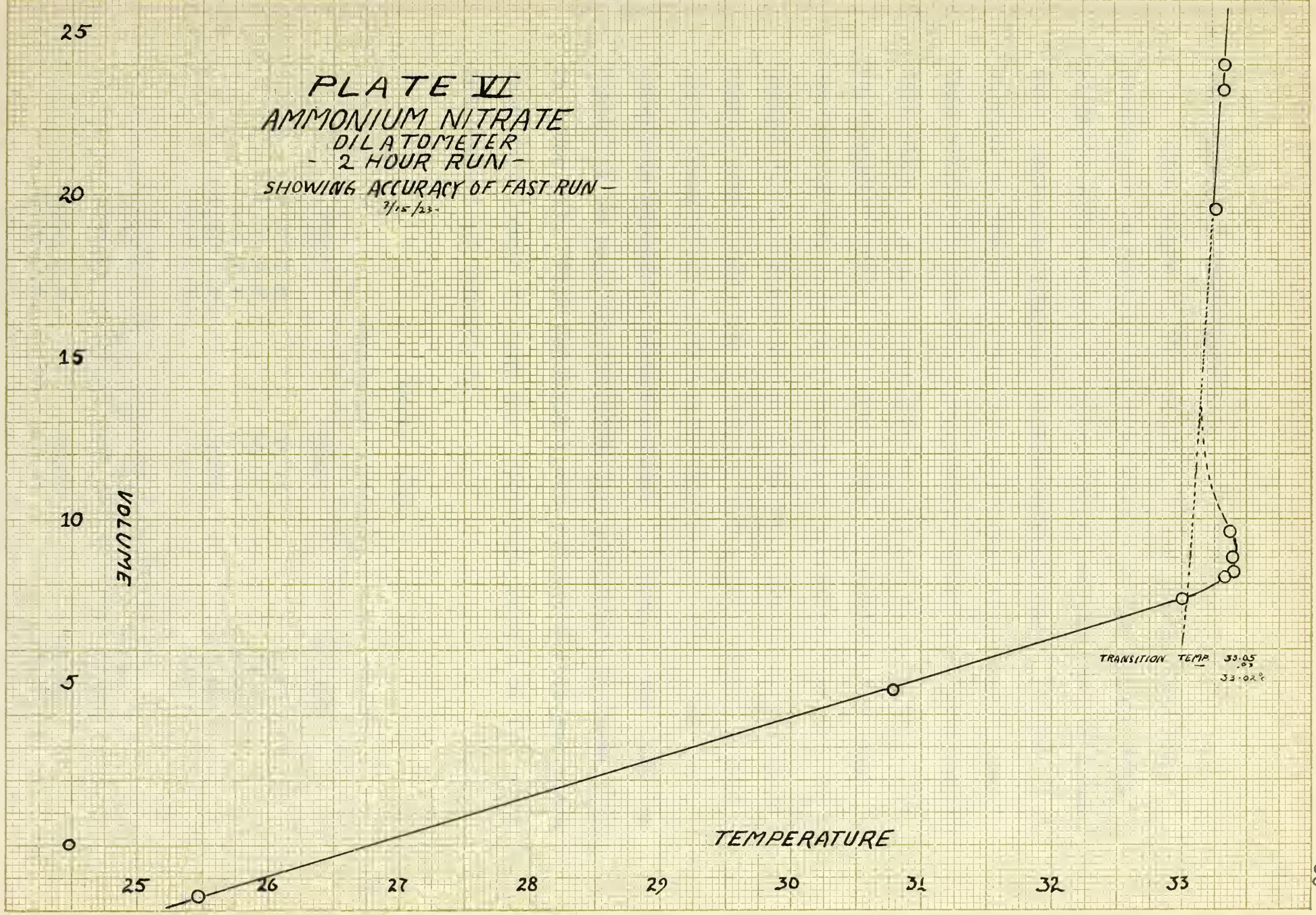
AMMONIUM NITRATE

DILATOMETER

- 2 HOUR RUN -

SHOWING ACCURACY OF FAST RUN —

3/15/23.



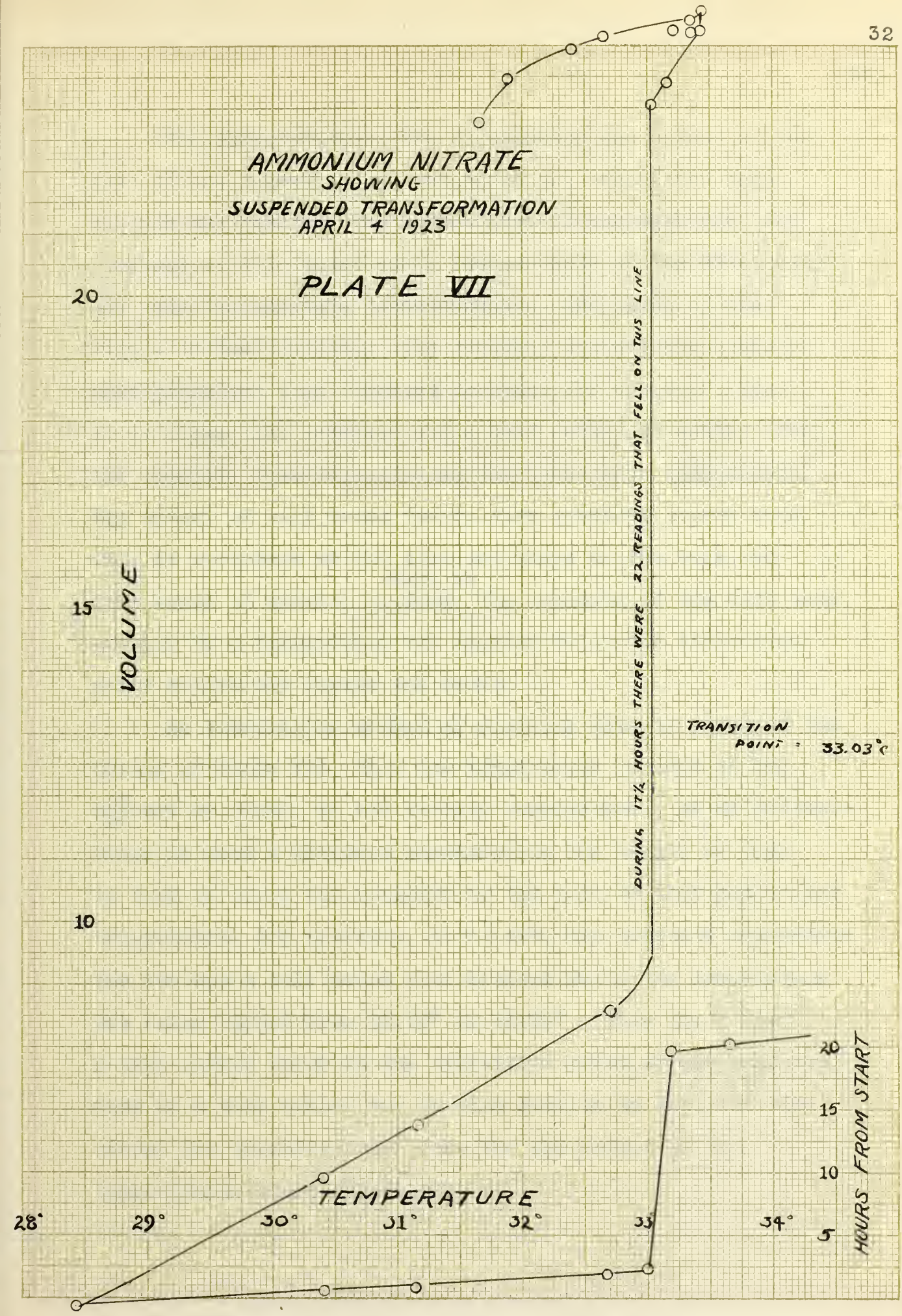
(6) Suspended Transformation.

The volume of the material in the bulb after the transition is that of the form stable at the higher temperature. With ascending temperatures, as soon as the transition point is reached, the few particles next to the surface of the bulb transform to occupy their new volume. This slight and gradual increase in volume must necessarily take place, as all the particles can not be brought to the same temperature at the same time. By plotting the temperature of the bath as it steadily increases, against the height of the liquid in the capillary tube as it gradually rises, none other than a sloping curve can result, and no exact transition point will be indicated. This slow and sometimes suspended transformation is shown in the curve on Plate VII on page 32. The data for this curve is shown below in Table VII. This experiment was carried out to ascertain just what length of time the transition needed at the exact temperature of transition.

Table VII.

Ammonium Nitrate.

TIME	TEMP.	VOLUME
3:00 P.M.	28.41	3.85
3:55 P.M.	30.40	6.00
4:55 P.M.	31.17	6.80
7:56 P.M.	32.70	8.60
8:14 P.M.	33.03	9.60
(22 readings from 8:14 P.M. April 19, to 1:00 P.M. April 20, all with the temperature at 33.03° are not recorded here.)		
1:00 P.M.	33.03	23.10
3:30 P.M.	33.45	24.80


AMMONIUM NITRATE
SHOWING
SUSPENDED TRANSFORMATION
APRIL 4 1923
PLATE VII
20
15
10
VOLUME
DURING 17¼ HOURS THERE WERE 22 READINGS THAT FELL ON THIS LINE
TRANSITION POINT = 33.03°C
TEMPERATURE
28°
29°
30°
31°
32°
33°
34°
20
15
10
5
HOURS FROM START

The temperature of the dilatometer was raised at the rate of one degree every hour until the transition temperature was reached. The temperature of the bath was held constant at this point until the contents of the dilatometer had made the complete transformation. The level of the liquid in the capillary rose steadily for seventeen and a half hours and then remained constant for one hour. Thus it is shown that seventeen and a half hours are needed for the complete transformation at the transition temperature, the amount of salt being twenty-five grams. Of course this time is dependent on the size and shape of the bulb. By four hours of gradual cooling, the contents of the bulb were brought to a temperature two degrees below the transition point before any change was noted.

An interesting method of plotting data is shown at the bottom of Plate VII. Here the temperature is used as the abscissa as usual. At any certain temperature , as an ordinate, there is used a distance representing the length of time it took to bring the contents of the bulb to that particular temperature. For instance, at 32.50°, the ordinate represents the two and a half hours that elapsed while the temperature was being raised from 28.25° to 32.50° . This curve shows a very marked break at the transition point, as was expected. This is a much better way to plot results to show the time needed for transformation than the old method of the temperature-volume relations.

(7) Thermometric Method.

In all the cases in the literature where this method was employed, it was used with either hydrated salts, or complex salts. This does not include the work on the elements such as sulphur and phosphorus, but only includes work on compounds. It was used in the present case on the compound ammonium nitrate, with success.

The apparatus suggested by van't Hoff [3] was tried, but did not give results that were desirable. The apparatus of van't Hoff, a test-tube, is as extremely simple as the apparatus of Richards[7] is extremely complicated. Richards had allowances made for the thermometer stem temperature, external and internal pressures, the 'fundamental-interval', the calibration correction, and many other slight and remotely possible sources of error. The apparatus used for the work on ammonium nitrate is shown in the sketch in Figure 4. The outer tube was sufficiently large that there was three-fourths of an inch of air between its walls and the test-tube inside with the ammonium nitrate. No stirring was possible with the dry salt, only an occasional tapping of the thermometer served as agitation. Heat was furnished by suspending the tube in the thermostat where the temperature was raised at the rate

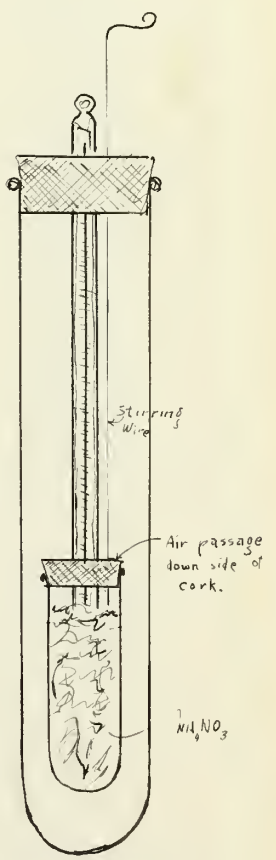


Figure 4

Table VIII.

Ammonium Nitrate. Heating Curves.

About 3mm. size.		Ground in mortar.	
Time	Temp.	Time	Temp.
10:40	32.47	2:12	30.74
10:53	33.00	2:52	31.45
11:00	33.20	3:28	33.01
11:02	33.22	3:32	33.18
11:03	33.22	3:39	33.45
11:04	33.23	3:43	33.58
11:05	33.23	3:44	33.60
11:06	33.23	3:45	33.60
11:07	33.23	3:46	33.61
11:08	33.23	3:47	33.61
11:09	33.23	3:48	33.61
11:10	33.23	3:49	33.60
11:11	33.23	3:50	33.57
11:12	33.23	4:01	33.17
11:13	33.22	4:03	33.10
11:14	33.22	4:07	33.05
11:15	33.20	4:12	32.98
11:16	33.18	4:15	32.96
11:21	33.09	4:16	32.95
11:28	32.99	4:17	32.94
11:29	32.98	4:18	32.93
11:30	32.98	4:20	32.92
11:31	32.97	4:22	32.94
11:32	32.97	4:23	32.95
11:33	32.96	4:24	32.95
11:35	32.96	4:25	32.95
11:36	32.96	4:26	32.95
11:37	32.96	4:27	32.95
11:39	32.96	4:28	32.96
11:40	32.96	4:29	32.97
11:41	32.97	4:31	33.00
11:42	32.98	4:34	33.00
11:45	33.01	4:36	33.02
11:54	33.09	4:40	33.04
12:01	33.11	4:58	33.20

of 2^{o} per hour from the heat of an electric lamp.

The effect of the size of particles of the salt in a determination may be seen from the curves on Plate VIII. (Data in Table VIII above.) The conditions for the two determinations were identical with the exception of the particle size. Where the salt was finely ground in a mortar,

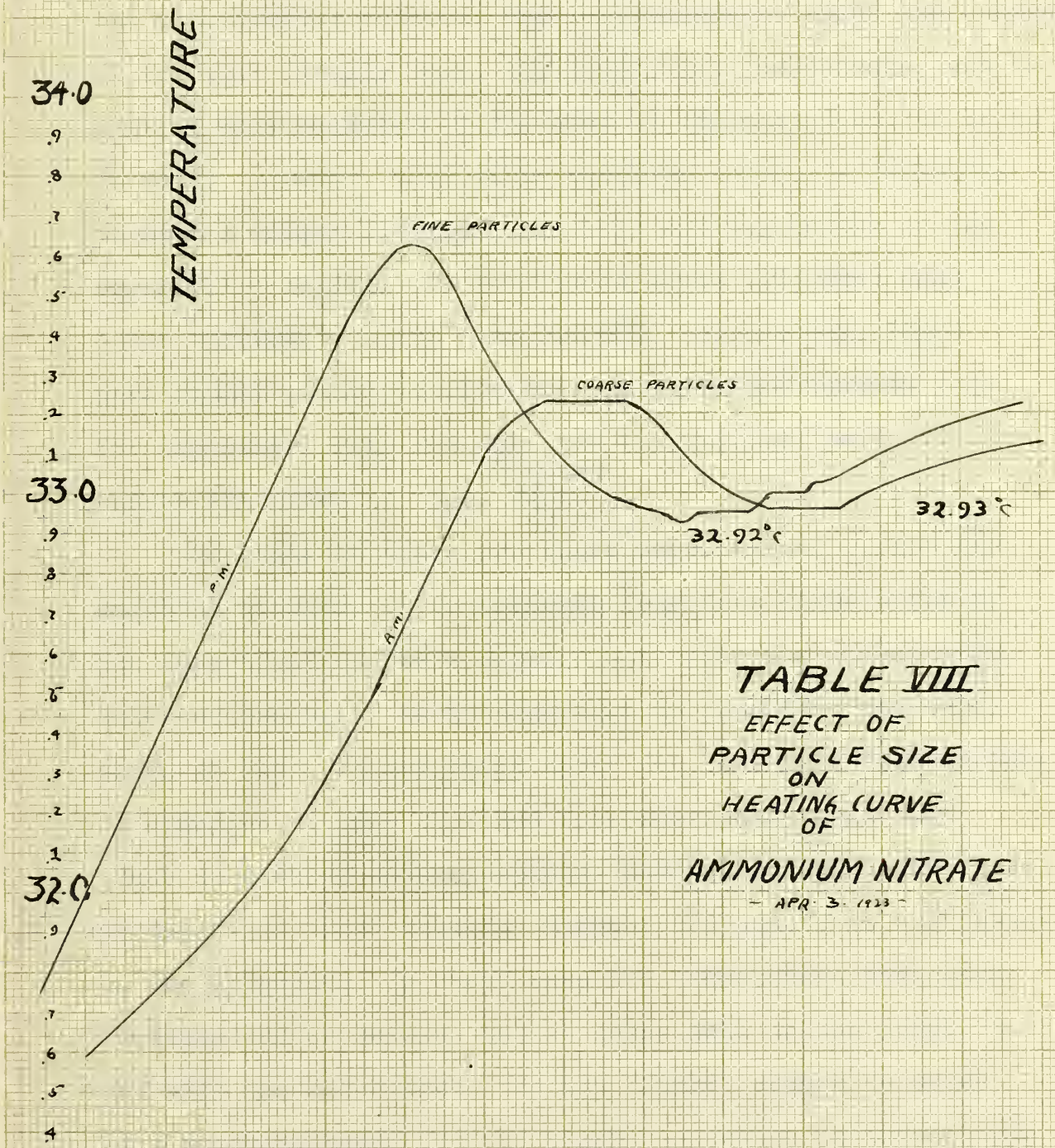


TABLE VIII

EFFECT OF PARTICLE SIZE ON HEATING CURVE OF

AMMONIUM NITRATE

– APR 3. 1923 –

TIME

ONE MINUTE FOR EACH SMALL SQUARE

the superheating amounted to nearly seven tenths of a degree, while where the particles were larger in size, only about half the superheating occured. The temperature to which the contents of the bulb finally fell, the transition temperature, was in neither case affected by the size of the particles. It is to be noted, however, that it is peculiar to coarse particles to have a slight flat part in their heating curves in the superheated region. The results in Plate VIII show very close agreement, 32.92° and 32.93°C. (corrected). There were eighty points to plot for one curve and seventy four for the other. Only the data for the critical parts of the curves are given in Table VIII.

On Plate IX there are three more heating curves for ammonium nitrate. It is apparent from this Plate which of the determinations were carried out using the coarse particles of the salt. It is important to note that the curve shown on Plate IX and dated April 5th. was made from the use of ammonium nitrate that had been previously used many times in similar determinations. Several attempts were made to duplicate these results without the use of an air-jacket on the apparatus. In every case the temperature indicated superheating as before, but it never fell to the level it did with the air-jacket. The air blanket seemed to serve as a shock-absorber for the slight variation in temperature and gave more accurate results.

(8) Conductivity Method.

It was not definitely known whether there were

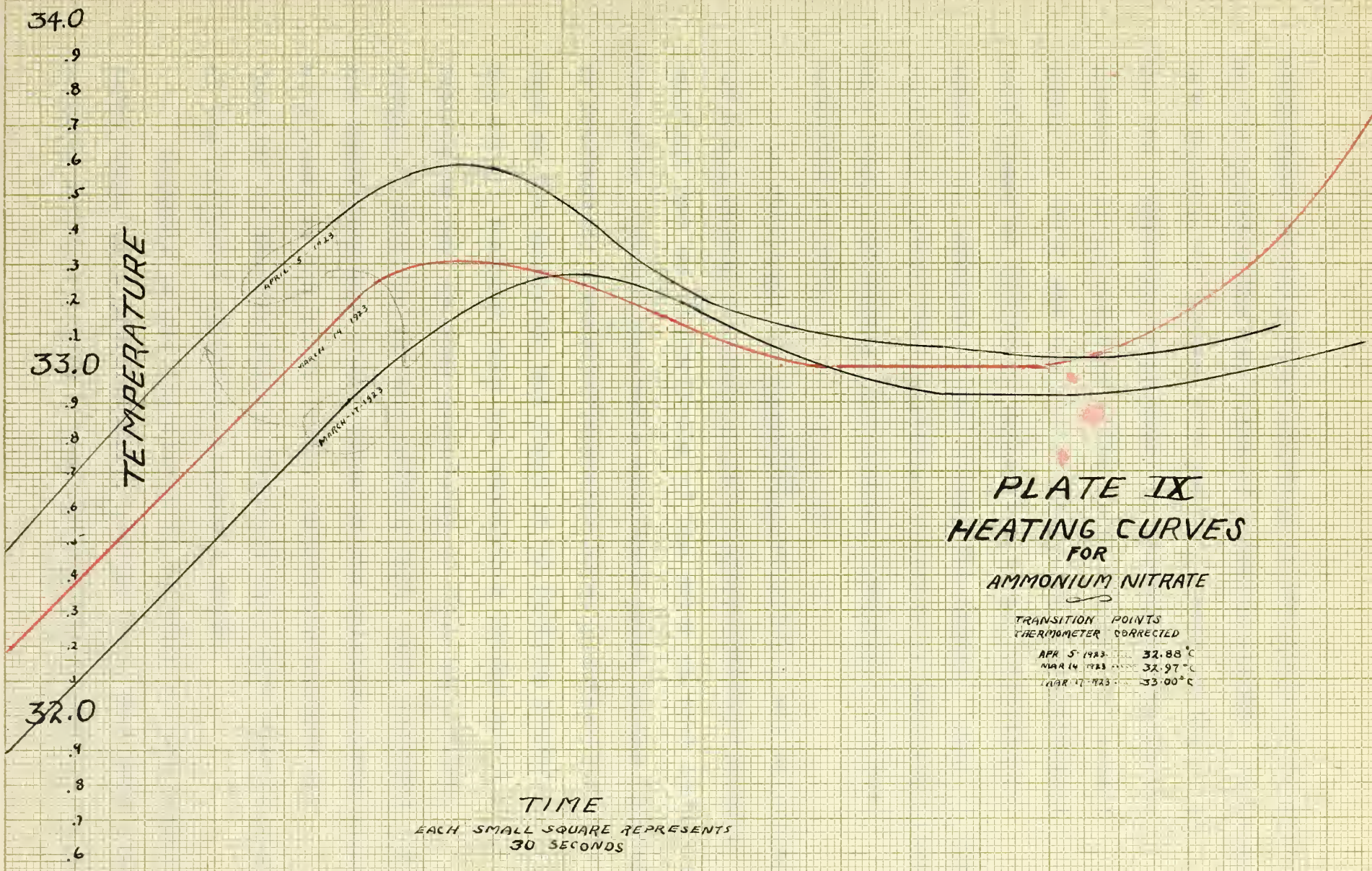


PLATE IX

HEATING CURVES FOR AMMONIUM NITRATE

TRANSITION POINTS
THERMOMETER CORRECTED

APR 5 1923	32.88 °C
MAR 14 1923	32.97 °C
MAR 17 1923	33.00 °C

polymorphic modifications existing in the state of solution, as for instance the two forms of ammonium nitrate, alpha and beta rhombic. Of course this question leads to the point, can the transition temperature be ascertained while the substance is in solution ? The first method that seemed worthy of trial was the one of measuring the equivalent conductance at different temperatures, and plotting it against the temperature and noting the general trend of the resulting curves. The following solutions of ammonium nitrate were used; 0.01 Normal, 0.1 Normal, 1.0Normal, and one saturated at 25°C.

In starting, the equivalent conductance was determined for a 0.1 Normal solution at 18° , after getting the cell constant and the conductivity of the water at that temperature. The value compared favorable with that given in the literature by Kohlrausch. (Landolt-Börnstein, Ed.4, p.1094. 1912.) As soon as the apparatus was found to be working properly, only the direct readings from the Wheatstone Bridge and the resistance box, in ohms resistance of that particular amount of solution in that certain cell, were recorded. If any transition would take place in the solution there would be a break in the curve of the temperature against any function of the resistance. Two such runs were made on each of the different solutions mentioned above.

In order to see the effect of solution on the transition temperature of a hydrated salt, similar runs were made using a tenth normal solution of the decahydrate of sodium sulfate.

The curves for these determinations are on Plate X, page 41, and the data in Table X below.

Table X.

Electrical Methods.

N/10 $Na_2SO_4 \cdot 10H_2O$

Time	Temp	Ext. Res.	X	1000-X	Cell Res.
9:30	25.00	52.60	500.0	500.0	52.60
1:15	25.05	53.00	502.0	498.0	52.59
1:30	26.95	50.60	500.0	500.0	50.60
2:08	29.00	48.30	499.0	501.0	48.58
2:45	31.85	46.00	500.0	500.0	46.00
3:10	33.90	44.20	500.0	500.0	44.20
3:40	35.90	42.60	500.0	500.0	42.60
4:05	38.00	41.80	505.2	494.8	40.85
		N/10 NH_4NO_3			
1:30	28.70	37.40	497.7	502.3	37.73
2:50	31.95	35.55	500.0	500.0	35.55
3:10	34.30	34.10	500.0	500.0	34.10
3:45	36.40	32.80	500.0	500.0	32.80
4:00	38.60	32.70	500.0	500.0	31.70
5:00	24.80	40.30	500.0	500.0	40.30

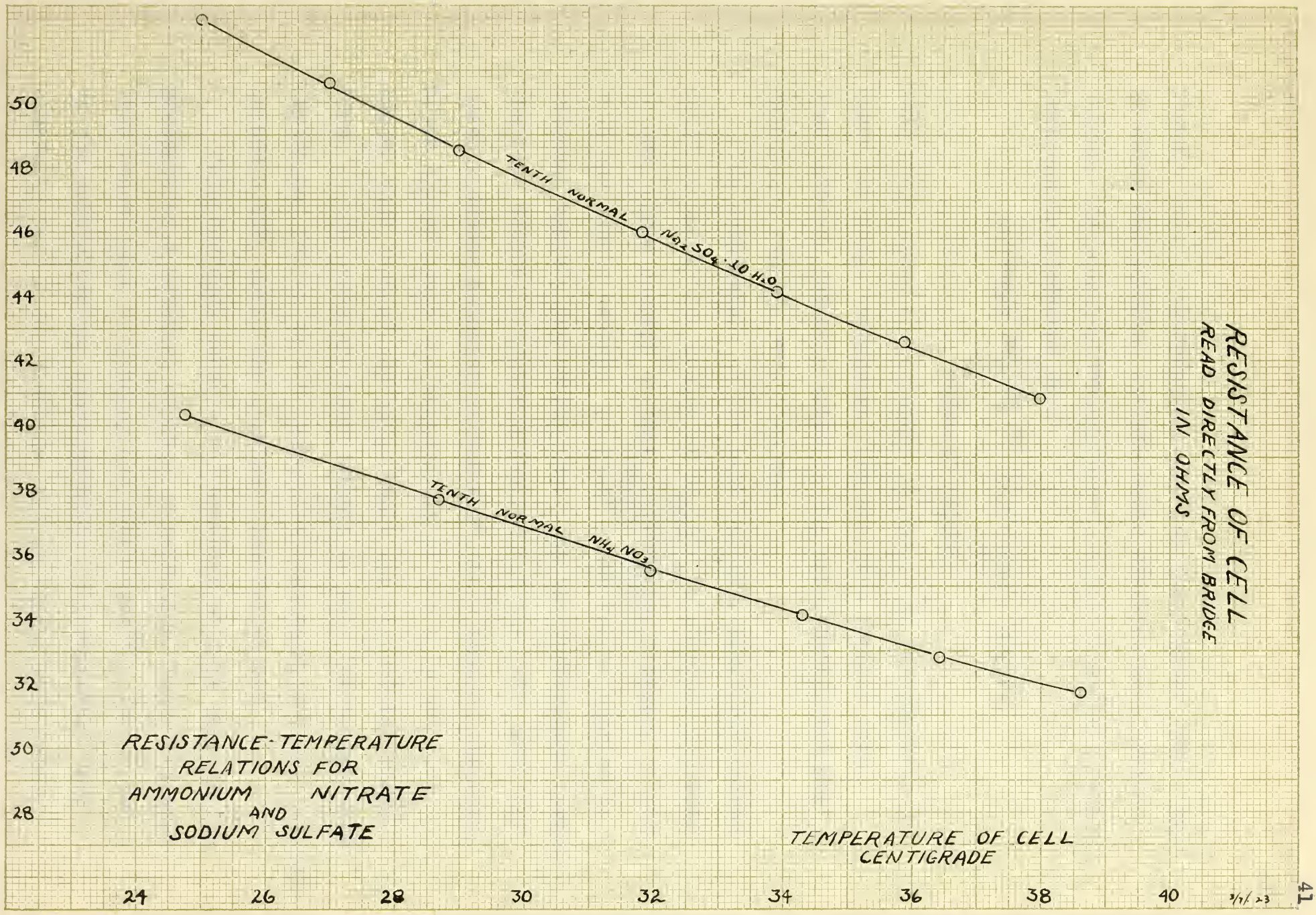
The curves plotted from the above data prove that in the state of solution, there is no method for the determination of transition points. When in aqueous solution, the polymorphs undergo definite hydration and their characteristics merge.

(9) Ammonium Nitrate and Ethyl Alcohol.

The equation for the transition of ammonium nitrate from the alpha to the beta rhombic, can be written as:-

$$\alpha \text{ rhombic } NH_4NO_3 \rightleftharpoons \beta \text{ rhombic } NH_4NO_3$$

It has been shown that this reaction takes place at a rather slow rate, that is, there is suspended transformation. It was


50
48
46
44
42
40
38
36
34
32
30
28
TENTH NORMAL $Na_2SO_4 \cdot 10\,H_2O$
TENTH NORMAL NH_4NO_3
RESISTANCE OF CELL
READ DIRECTLY FROM BRIDGE
IN OHMS
RESISTANCE-TEMPERATURE
RELATIONS FOR
AMMONIUM NITRATE
AND
SODIUM SULFATE
TEMPERATURE OF CELL
CENTIGRADE
24
26
28
30
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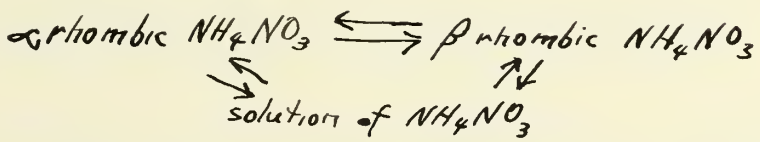
3/7/23

thought that by introducing into the dilatometer some liquid in which the ammonium nitrate would dissolve to a limited extent, the reaction would proceed to the right more rapidly. This can be expressed as: -



This would allow the solution to act as an intermediary and cause the rapid conversion into the beta rhombic form. When this was actually tried in the dilatometer, the most surprising results were obtained.

The temperature of the bath was very carefully raised until it was in the region of 33.00°. No abnormal increase in the volume occured at this temperature, however, so the bath was slowly heated. At 34.0° C the volume started to increase rapidly and at the same time the temperature inside the bulb dropped slightly below that of the bath, and then quickly dashed on until it was 1.2° above that of the bath. After eleven hours the temperature of the bulb was 1.6° higher than that of the bath, while the alcohol had risen 52cm. in the capillary tube. Within an hour the temperature inside had fallen to 2.6° below its high mark, and the bath had gained 0.52°, while the capillary had fallen 8cm.

This unsteady behavior of ammonium nitrate when in the presence of a material capable of oxidation, bears out some very recent work by Findlay and Rosebourne[20]. The contents of the bulb after the above mentioned determination were carefully tested for aldehyde, but no traces were found.

While pure ammonium nitrate was fairly stable at 100° C , it evidently becomes very unstable in the presence of a material such as ethyl alcohol, at temperatures very much lower. Time did not permit the further study of the problem that has made itself evident in this connection.

(10) The Effect of Urea on the Transition of Ammonium Nitrate.

Richards recommends the transition temperature of $Na_2SO_4 \cdot 10H_2O$ as a fixed point in the calibration of thermometers. He gives the transition temperature as being exactly 32.384°C. It is not an easy matter to obtain this temperature, especially without the aid of Richards' elaborate apparatus. The salt has to be prepared very carefully just before the determination, as any change in the hydration would give worthless results. In a practical sense, the reaction is not reversible, that is there is never an opportunity in either the dilatometer or in the thermometric method, for the complete contact necessary for the proper re-hydration from the liquid and the solid phase. Would not a salt, that is in the anhydrous condition at ordinary temperatures, and that gives transition phenomena, be better for giving reliable results for the calibration of thermometers ? Ammonium nitrate gives all the desirable properties for such work. Its transition temperature is in the region where a good fixed point is needed. If, by the addition of an impurity, the temperature could be altered, there would result a very useful mixture. By calculation, it could be found how much of an impurity to

add to make the transition take place at any desired point within that region.

It has been shown that an isomorphous substance will elevate the temperature of transition. In an endeavor to get a lowering, urea was added to a dilatometric determination with ammonium nitrate. NO TRANSITION POINT COULD BE OBSERVED IN THIS CASE. With this mixture, no transition point could be found by the thermometric method. The peculiar fact about this mixture was that when the dry materials were placed together inthe air, there was some reaction, as there soon appeared a solid phase with a liquid phase above. A sample of ammonium nitrate, carefully freed from water, was mixed with a sample of urea which had been dried at 120° in an electric oven, and the mixture placed immediately in a vacuum dessicator. By this method, and with the aid of small capillary tubes, it was hoped to obtain a melting point - composition curve of various mixtures of the two materials. As soon as the mixtures were taken out and slightly warmed, the reaction occured, and soon the whole mass in the dessicator was pasty.

It is not known just exactly what occured.It is evident that there was some change taking place. Water appeared, either from the atmosphere by virtue of the newly acquired hydroscopic property of the mixture,or by elimination from the two substances during a chemical reaction. By carefully weighing the separate components and the resulting products, it could be shown where the moisture entered. The ammonium

nitrate could have accelerated the conversion of the urea into some of its various related compounds with the splitting out of water. At any rate this dry reaction between the two materials hindered the intended use of the urea, but at the same time it has shown the importance of further research.

(11) The Effect of Sodium Nitrate on the Transition of Ammonium Nitrate.

In the preceeding section mention was made of the effect of impurities on the transition temperature. It has been known for many years that the addition of a heteromorphous substance would lower the transition temperature, while if the substance was isomorphous, the temperature would be elevated. Richards [7] uses the following relation in calculating the effect of impurities.

$$\text{Heat of transition} = \frac{(\text{mols. impurity})RT^2}{(\text{mols. solvent salt})dT}$$

On Plate V there are two curves showing the effect of sodium nitrate on ammonium nitrate. By using the values from Romanese [19], this relation holds fairly well for the case with isomorphous materials. The curves on Plate V show exact checks on the elevation of the temperature, which was 0.340° when the salts were in the proportion indicated on the Plate. This behavior may be construed to indicate that sodium nitrate is isomorphic or isodimorphic with ammonium nitrate. This could be expected, however, from the relative positions of the two substances, sodium and ammonium in Arzruni's

Isomorphous Series [21]. During the past year Lowry and Early[22] have made a very careful study of the systems, $NaNO_3$- NH_4NO_3 and NaCl- NH_4NO_3 .

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V. DISCUSSION OF NUMERICAL RESULTS.

A summary of all the work done on ammonium nitrate that throws light on the transition temperature, is shown in Table XII.

Table XII.

Date	Method	Length of Run	Temperature.
Oct.19, 1922	Dilatometric	25 Hours	33.05°C
Oct.23, 1922	Dilatometric	27 "	33.02
Dec. 6, 1922	Dilatometric	7 "	33.15
Mar.14, 1923	Thermometric	3 "	32.97
Mar.17, 1923	Thermometric	3 "	33.00
Mar.15, 1923	Dilatometric	2 "	33.02
Apr. 3, 1923	Thermometric	3 "	32.92
Apr. 3, 1923	Thermometric	3 "	32.93
Apr. 5, 1923	Thermometric	3 "	32.88
Apr.17, 1923	Dilatometric	6 "	33.07
Apr.19, 1923	Dilatometric	29 "	33.03
	AVERAGE OF TRANSITION TEMPERATURES		33.00°C

Average by Dilatometric Method.... 33.06°C
Average by Thermometric Method.... 32.94°C.

The general average of the results is 33.00°C. This average value is not to be taken as the true transition temperature, however. It is to be noted that the averages from the different methods are different. All the results obtained by the dilatometer ran over 33.00°C , while none of the thermometric results ever gave a value over 33.00°C. This startling fact gives just reason for suspecting the validity of the grand average of all the results.

No attempt will be made here to prove either set of results, although it may be mentioned, however, that the thermometric method gives much less possibility of error than does the dilatometric method as employed in this work, due to the differences in reading temperatures. The fundamental principles underlying the two methods allow perfect checks in the results, making any discrepancies due to faulty apparatus. When this difference in results was noticed, the thermometers were again compared to a standard in the manner described in Part IV, and their corrections were found to be the same as found in the start of the work. The writer would prefer to call the true temperature of transition 32.94°C, but will have to wait until further work has been done before making the statement definite.

VI. SUMMARY

1. Six general methods for the determination of transition points were discussed.
2. A survey of the chemical literature revealed the fact that the transition temperature of alpha to beta rhombic ammonium nitrate was not definitely known.
3. Through an endeavor to accurately determine this transition temperature, it was found that the type of dilatometer described in the literature is difficult to make, cumbersome to use, and inaccurate.
4. A new form of dilatometer was described.
5. It was shown why a thermometer was necessary inside the dilatometer bulb to avoid thermal lags.
6. A stopcock is very desirable in the bulb of the dilatometer described, for the following reasons:
   (a) It permits the bulb to be filled without the usual heating and cooling, thereby increasing the usefulness of the instrument.
   (b) Bubbles that may form are caught without escaping through the capillary to give errors.
   (c) It permits a short scale to be used for any temperature range.
   (d) It makes possible the filling of the bulb at room temperature for a high temperature determination.
7. A dye was used in the dilatometer liquid to aid in reading the level in the capillary tube, and no change in the transition temperature resulted.

8. When a mixture of two polymorphic forms is put into aqueous solution, the separate characteristics merge, and no transition point can be determined.

9. 0.216 mols. of sodium nitrate per mol. ammonium nitrate gives a transition point 0.340°C higher than that of pure ammonium nitrate, indicating the isomorphic relations of the two salts.

10. In the presence of easily oxidizable material such as ethyl alcohol, ammonium nitrate gives no transition point, but behaves in a very capricious manner.

11. Ammonium nitrate with urea as an impurity, does not show the usual transition. Dry mixtures of the two substances soon become pasty and show evidences of some chemical reaction. A study of the properties of the system, urea-ammonium nitrate, would offer very interesting possibilities.

12. The probable transition temperature of ammonium nitrate from the alpha rhombic to the beta rhombic has been shown to be 32.94°C.

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